Designation: C1254 – 13

Standard Test Method for Determination of Uranium in Mineral Acids by X-Ray Fluorescence[1]

This standard is issued under the fixed designation C1254; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the steps necessary for the preparation and analysis by X-ray fluorescence (XRF) of mineral acid solutions containing uranium.

1.2 This test method is valid for those solutions containing 0.05 to 20 g uranium/L as presented to the spectrometer. Higher concentrations may be covered by appropriate dilutions.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 9 and Note 1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials

C982 Guide for Selecting Components for Energy-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2008)[3]

C1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2011)[3]

D1193 Specification for Reagent Water

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

2.2 *Other Document:*

ANSI/HPS N43.2–2001 Radiation Safety for X-ray Diffraction and Fluorescence Analysis Equipment[4]

3. Terminology

3.1 *Definitions:*

3.1.1 See Terminologies E135 and C859 for definitions of terms applicable to this test method.

4. Summary of Test Method

4.1 Solution standards containing 0.025 g uranium/L to 20 g uranium/L and an appropriate internal standard (usually either yttrium or strontium), unless a scatter line is used in lieu of, are placed in a liquid sample holder of an X-ray spectrometer and exposed to an X-ray beam capable of exciting the uranium L-alpha emission line and the appropriate emission line for the internal standard (usually the K-alpha line). The intensities generated are measured by an appropriate detector. The intensity ratio values obtained from this data are used to calibrate the X-ray analyzer.

5. Significance and Use

5.1 This test method is applicable to aqueous solutions of uranium containing 0.05 to 20 g uranium per litre of solution presented to the spectrometer.

5.2 Either wavelength-dispersive or energy-dispersive X-ray fluorescence systems may be used provided the software accompanying the system is able to accommodate the use of internal standards.

6. Interferences

6.1 This test method requires the use of an appropriate internal standard. Care must be taken to ascertain that samples analyzed by this test method do not contain the internal standard element or that this contamination has been corrected for mathematically whenever present. Such corrections are not addressed in this test method.

6.2 Alternatively a scatter line may be used as internal standard in which case the preparation of internal standard

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from the Health Physics Society, McLean, Virginia, 22101.

solutions and subsequent doping of samples and calibration standards is unnecessary.[5]

6.3 Sample must not contain significant concentration of any elements that have mass absorption edges that fall between the energies of the uranium L-alpha line and the internal standard line.

6.4 Care must also be taken that the choice of internal standard and sample medium are compatible; that is, do not use yttrium with solutions containing HF or strontium with those having H_2SO_4.

7. Apparatus

7.1 *X-Ray Spectrometer*—See Guide C982 or Guide C1118 for the selection of the X-ray spectrometer. This test method is valid for either energy-dispersive or wavelength-dispersive systems.

7.2 *Sample Cups:*

7.2.1 Prepare liquid sample cups for the X-ray spectrometer as described by the manufacturer. Vented, disposable sample cups with snap-on caps are satisfactory for most such analyses; such cups decrease the likelihood of contamination between samples.

7.2.2 Polyester, polyethylene, and polypropylene films have been used successfully as the film window for such cups. Tests should be performed to determine the serviceability of any film chosen before insertion into the instrument.

7.3 *Solution Dispenser*—The dispenser for the internal standard solution should be capable of reproducibly dispensing the internal standard to a level of 0.5 % relative standard deviation of the volume dispensed.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Specification D1193.

8.3 *Ferric Nitrate,* $Fe(NO_3)_3 \cdot 9H_2O$.

8.4 *Nitric Acid,* HNO_3, concentrated (70 %).

8.5 *Strontium Carbonate,* $SrCO_3$.

8.6 *Uranium Oxide,* U_3O_8, NBL CRM-129[7] (or equivalent).

8.7 *Yttrium Oxide,* Y_2O_3.

9. Technical Precautions

9.1 XRF equipment analyzes by the interaction of ionizing radiation with the sample. Applicable safety regulations and standard operating procedures must be reviewed prior to the use of such equipment. All modern XRF spectrometers are equipped with safety interlocks to prevent accidental penetration of the X-ray beam by the user. Do NOT override these interlocks without proper training, or a second knowledgeable person present during such operation. (See ANSI/HPS N43.2–2001.)

9.2 Instrument performance may be influenced by environmental factors such as heat, vibration, humidity, dust, stray electronic noise, and line voltage stability. These factors and performance characteristics should be reviewed prior to use of this standard.

10. Preparation of Apparatus

10.1 *Chamber Environment*—The standards and samples used in this test method are corrosive liquids. Some fumes will be emitted from the sample cups. These fumes may be detrimental to the spectrometer chamber. It is desirable to flush this chamber with an appropriate gas (for example, helium and nitrogen) before and during analysis. Some X-ray spectrometers control the change of sample chamber atmosphere (air, vacuum, helium, nitrogen) automatically through the software; in others, it must be done manually. Follow the instrument manufacturer's recommendations to achieve the inert gas environment.

NOTE 1—**Caution:** Allow sufficient stabilization time before analysis. Care must be taken to ensure that a vacuum environment is not chosen with liquid samples.

10.2 *X-Ray Power Supply*—If the power to the X-ray tube is not controlled by the instrument software, set the proper combination of voltage and current for the instrument in use. These settings must be determined by the user for his instrument and choice of X-ray tube. Allow sufficient stabilization time prior to analysis.

11. Calibration and Standardization

11.1 *Internal Standard Solution* (25.0 g/L):

11.1.1 Weigh 25 g of the chosen internal standard compound into an 800-mL beaker. Cover with water. Add concentrated nitric acid slowly. For yttrium oxide the reaction will be slow and may require heating. For strontium carbonate, the reaction will be vigorous.

11.1.2 Heat on a hot plate if necessary to complete the dissolution.

11.1.3 Cool the solution to room temperature, and transfer to a 1000-mL volumetric flask. (Filter the solution if necessary.) Dilute to volume with water and mix thoroughly.

11.2 *Impurity Stock Solution (Optional):*

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[5] Andermann, George, and Kemp, J. W., "Scattered X-Rays as Internal Standards in X-Ray Spectroscopy," *Analytical Chemistry*, Vol. 20(8), 1958.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[7] Available from the U.S. Department of Energy, New Brunswick Laboratory, D350, 9800 South Cass Avenue, Argonne, IL 60439, Attn: Reference Material Sales.

11.2.1 Weigh 50 g of reagent grade ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, into a 600-mL beaker.

11.2.2 Dissolve the crystals in 200 mL of water and 50 mL of concentrated nitric acid.

11.2.3 When cool, transfer the solution to a 1000-mL volumetric flask and dilute to volume with water.

11.3 *Uranium Calibration Standards:*

11.3.1 Prepare a uranium standard for each concentration level by weighing into a 150-mL beaker the amounts of uranium oxide given in Table 1.

11.3.2 Dissolve the oxide in 25 mL of water and 25 mL concentrated nitric acid. Heat on a hot plate, if necessary to complete the dissolution.

11.3.3 When cool, transfer each solution to a properly labeled 100-mL volumetric flask. Add the amount of internal standard solution and impurity solution (if desired) indicated in Table 1 to each volumetric flask.

NOTE 2—The internal standard solution may be added using a dispensing pipet if desired. However, care must be taken to ensure that no adjustment to the dispenser is made between use for standards and use for samples.

11.3.4 Dilute to volume with water and mix thoroughly.

11.4 *Instrument Calibration:*

11.4.1 Follow manufacturer's instructions for the instrument in use to obtain intensity data for the uranium L-alpha and the internal standard line or scatter line for each standard.

11.4.2 Exercise care that the analytical conditions determined appropriate for the instrument in use are documented, or recorded, in sufficient detail that these may be reproduced in subsequent runs and when analyzing the samples.

11.4.3 Calculate the uranium/internal standard ratios from the data obtained in 11.4.1. Calculate a calibration curve using these ratios. Currently available instrument software should need curve equation. A complete discussion of the mathematical derivation of the available equations is outside the scope of this procedure. Explanations of correction models and interelement effects are found in several sources.[8,9]

TABLE 1 Uranium Calibration Standards

Concentration, (g/L)	Weight U_3O_8 (CRM-129)[A]	Internal Standard, (mL)	Impurity Solution, (mL)[A]	Final Volume, (mL)
0.025	0.00295	4	5	100
0.050	0.00590	4		100
0.100	0.01180	4	5	100
0.500	0.05898	4		100
1.000	0.11796	4	5	100
1.250	0.14745	4		100
1.500	0.17694	4	5	100
1.750	0.20644	4		100
2.00	0.23593	4	5	100
4.00	0.47185	4		100
6.00	0.70778	4	5	100
8.00	0.94370	4		100
10.00	1.17963	4	10	100
12.00	1.41556	4		100
14.00	1.65148	4	10	100
16.00	1.88741	4		100
18.00	2.12333	4	10	100
20.00	2.35926	4		100

[A] Weights will need to be adjusted for the purity of the uranium reference material used. See the certification accompanying the material. Weights indicated are for NBL CRM-129 (no longer available; use NBL CRM-129 or equivalent). Use of the impurity solution is optional.

12. Procedure

12.1 *Sample Preparation:*

12.1.1 Shake the sample and pipet an appropriate aliquot into a tared 50-mL volumetric flask.

NOTE 3—Some estimate of the approximate g U/L will be necessary to determine the appropriate dilution. This may be obtained by gamma counting of the incoming sample, prior knowledge of the origin of the sample or some other scheme devised by the user. Such schemes are outside the scope of this standard.

12.1.2 Obtain the gross weight of the sample and flask. (If an answer on a weight basis is not desired, this may be omitted.)

12.1.3 Add 2 mL of the internal standard solution; dilute to volume with water and mix thoroughly.

12.2 *Counting the Sample:*

12.2.1 Set the X-ray spectrometer to the conditions noted in 11.4.1. If the analytical conditions are controlled by computer, start the computer according to manufacturer's instructions for the software in use.

12.2.2 Shake each flask to mix thoroughly. Fill the liquid sample cup with the appropriate amount of sample (cup and volume both consistent with that used in 11.4.2 for calibration).

12.2.3 Following manufacturer's instrumental instructions, obtain intensities for the uranium L-alpha line and the internal standard or scatter line.

12.2.4 Calculate the uranium concentration in the flask using the appropriate equation.

NOTE 4—Additional factors, such as volume, weight, isotopic correction, secondary dilutions, may be included in the utilized equations to obtain results on the proper basis for the user's application.

13. Precision and Bias

13.1 There is no readily available certified material (uranium dissolved in mineral acid) for this test method. However, two solutions of NBL CRM-114[10] (U_3O_8) were prepared.

13.1.1 The first solution, with a theoretical value of 0.03916 g uranium per g solution (g U/g solution), corresponding to ~42.4 g U/L, was prepared by dissolving ~50 g (weighed to the nearest 0.1 mg) as outlined in 11.3.2 and transferring to a tared 1000–mL volumetric flask. This solution was diluted to volume with water, mixed thoroughly and weighed. Aliquots of this solution were prepared by five different technicians and analyzed on two different X-ray spectrometers over a four-month period. The average of 30 determinations (see Table 2 for data) was 0.03923 g U/g solution, a relative difference of 0.27 % from the theoretical value, with a relative standard deviation of 0.53 %

13.1.2 The second solution, with a theoretical value of 0.000984 g uranium per gram solution, corresponding to ~0.1

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[8] Bertin, Eugene P., *Introduction to X-Ray Spectrometric Analysis*, Plenum Press, New York and London, 1978.

[9] Tertian, R., and Claisse, F., *Principles of Quantitative X-Ray Fluorescence Analysis*, Heyden and Son, London, Philadelphia, and Rheine, 1982.

[10] No longer available; see Table 1, Footnote A.

g U/L, was prepared by dissolving ~0.59 g (weighed to the nearest 0.1 mg) as outlined in 11.3.4 and transferring to a tared 500–ml volumetric flask. This solution was diluted to volume with water, mixed thoroughly and weighed. Aliquots of this solution were prepared by nine different technicians and analyzed on two different X-ray spectrometers over a seven-month period. The average of 30 determinations (see Table 3 for data) was 0.000987 g U/g solution, a relative difference of 0.35 % from the theoretical value, with a relative standard deviation of 1.79 %.

13.1.3 The t-test for bias as described by Youden[11] was applied to each set of data. It indicated no significant bias in either set.

14. Keywords

14.1 mineral acid; uranium; X-ray fluorescence (XRF)

TABLE 2 Data for Solution #1

NOTE 1—Uranium in Mineral Acid by XRF
Theoretical value 0.03916 g U/g solution.

0.039178
0.039669
0.039574
0.039480
0.038924
0.039356
0.038952
0.038976
0.039405
0.038952
0.039313
0.038925
0.039126
0.039138
0.039213
0.039356
0.039331
0.039418
0.039241
0.039190
0.039640
0.039210
0.038910
0.039133
0.039320
0.039198
0.039291
0.039100
0.039143
0.039123
$\bar{X}$ = 0.039226
s = 0.000208

TABLE 3 Data for Solution #2

NOTE 1—Uranium in Mineral Acid by XRF
Theoretical value 0.000984 g U/g solution.

0.0010027
0.001019
0.001006
0.00995
0.000959
0.00998
0.000987
0.000994
0.000989
0.000977
0.000988
0.000965
0.000985
0.000983
0.000982
0.000948
0.000984
0.000962
0.000974
0.001017
0.000996
0.000994
0.000994
0.000968
0.000979
0.001002
0.000976
0.001002
0.000989
0.000984
$\bar{X}$ = 0.000987
s = 0.000018

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[11] Youden, W. J., and Steiner, E. H., *Statistical Manual of the AOAC*, AOAC International, 1987.

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